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New Equation of State for DC745U

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We describe the construction of a new equation of state for the silicone elastomer DC745U. The EOS is calibrated to thermal, thermomechanical, and plate impact data taken at both room temperature and 60°C. The new EOS is generated in tabular form, as developmental SESAME 97990.

Keywords: equation of state, Hugoniot, silicone elastomers, DC745U

I. INTRODUCTION

DC745U is a silicone elastomer used in numerous parts of weapon systems, including as aft cap support in the W80 and as a pressure pad in the B61.^{1–7} In spite of this, the current SESAME library contains no entry for DC745.

DC745U crystallizes with $\sim 40\%$ crystallinity at around -50°C .^{6,7} This transition affects many features, including its shock compressibility.⁷ The new EOS is based in part on room temperature shock data digitized from Ref. 4, but does well in reproducing additional shock data taken at -60°C .⁸

II. EQUATION OF STATE

A. Methods

The new EOS was based on the SESAME decomposition of the Helmholtz free energy,

$$F(\rho, T) = \phi(\rho) + F_i(\rho, T) + F_e(\rho, T), \quad (1)$$

where $\phi(\rho)$ is the 0K energy of the static lattice (cold curve), F_i is the free energy due to ionic motion, and F_e is that due to thermal excitation of the electrons. Table I contains the basic EOS inputs, based on an elemental composition obtained from Ref. 1 and the ambient density reported in elsewhere.⁸ The EOS was constructed using a modified version of `OpenSesame-1.4.4`, the nature of the modifications being described below.

The cold curve was calculated based on fitting the room temperature shock data⁴ to

$$U_S = c_0 + s_1 u_p + s_2 u_p^2. \quad (2)$$

TABLE I. Basic EOS parameters for SESAME 97990.

Formula	C _{2.083} H _{6.029} SiO
Z(-e)	4.008
A (g/mol)	7.43494
ρ_0 (g/cc)	1.312

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Combined with the assumption of Mie-Grüneisen behavior,⁹ a Hugoniot fit to (2) can be used to extract the cold curve in tabular form.¹⁰ This result was bounded above and below by Thomas-Fermi-Dirac (TFD) theory^{11–13} and a “Lennard-Jones” model of the form¹⁴

$$\phi(\rho) = a_1 \rho^{a_2} - a_3 \rho^{a_4} + E_0, \quad \eta < \eta_o, \quad (3)$$

respectively. Values were supplied for a_4 and the cohesive energy E_{coh} , related to E_0 via¹⁵

$$E_{\text{coh}} = E_0 + \phi(\rho_0) + E(\rho_0, 0) \quad (4)$$

for the Grüneisen Γ models implemented in `OpenSesame`.¹⁶ The final term on the right hand side is simply the zero point energy. Additional parameters were adjusted automatically by `OpenSesame` to ensure continuity of the energy and its first two ρ derivatives at the match compressions η_o and η_{hi} , where $\eta = \rho/\rho_0$. Calibration of the parameters in (2) were based roughly on a least squares fit to plate impact data at ambient temperature,¹⁷ adjusted slightly to better match all the other data. Parameters for the cold curve at compressions $\eta < \eta_o$ were set largely in order to match thermal expansion data presented below.

The ionic contribution, F_i , was calculated using the Tarasov model.¹⁸ This model is a generalization on the standard Debye model, enabling multiple characteristic temperatures Θ based on oscillators in 1-3 dimensions. The generalization of the Tarasov model coded in `OpenSesame` replaces the Debye model for each theta with the JDNUC model¹⁹ which interpolates between the Debye model at low temperature and ideal gas behavior at high temperature. JDNUC assumes a Lindemann melt law²⁰ to determine the switch between Debye and ideal gas behaviors and allows a specific heat jump at melt, where for the current material the model melt behavior approximately captures decomposition.

The density-dependence of the characteristic temperatures (assumed to be the same in all cases) was incorporated through the Grüneisen parameter, which was modeled as

$$\Gamma(\rho) = \begin{cases} \Gamma_\infty + g_1(\frac{\rho_g}{\rho}) + g_2(\frac{\rho_g}{\rho})^2, & \rho \geq \rho_g \\ \Gamma_0 + g_3(\frac{\rho}{\rho_g}) + g_4(\frac{\rho}{\rho_g})^2, & \rho \leq \rho_g. \end{cases} \quad (5)$$

The match point was chosen to be the reference density ($\rho_g = \rho_0$) for simplicity, Γ at zero and infinite density

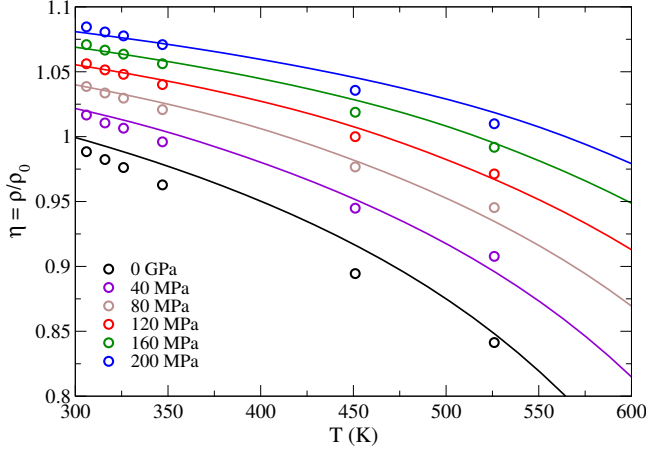


FIG. 1. Thermal expansion results for SESAME 97990 compared with data collected by Datapoint Labs. The data were for material of initial density $\rho_0 = 1.291$ g/cc, slightly different from the reference density of $\rho_0 = 1.312$ g/cc used in the SESAME table.

(Γ_0 and Γ_∞) were set to their theoretical values, and its left and right log derivatives (Γ'_L , Γ'_R) at the match point were set to $-\Gamma_g$ (consistent with $\rho\Gamma = \text{const}$). The value of Γ_g itself was then tuned to fit data.

The free energy of electronic excitations, F_e , was calculated based on Thomas-Fermi-Dirac theory. Electronic contributions to the energy and pressure are essentially negligible ($< 1\%$ at $P = 50$ GPa on the Hugoniot) over the $\rho - T$ domain for which there are data.

B. Results

The ionic portion of the EOS was calibrated to specific heat data taken from 213 to 343 K.²¹ The agreement (not shown) is excellent, although the limited range of the data somewhat obscures the complex character of thermal response in a polymer such as DC745. Generalization of the standard Debye model was essential for achieving the level of agreement obtained.

Similar comments apply to the thermal expansion results of Figure 1, where the EOS is plotted against isobaric data collected by Datapoint Labs²² on material of initial density $\rho_0 = 1.291$ g/cc. Results are plotted in terms of compression rather than density in order to normalize for the small difference in ρ_0 . By the standard of typical NNSA applications, the applied stresses depicted are quite small. Agreement of the EOS with the data is worst at ambient pressure, whereupon heating it also ventures deepest into expansion. Given the coarseness of our expansion models, this feature is perhaps not surprising.

Figures 2 and 3 illustrate calculated Hugoniots in the $U_S - u_p$ and $P - \rho$ planes. Agreement is good even for the cold data, in spite of the fact that they played only a minimal role in calibration of the EOS. There is some

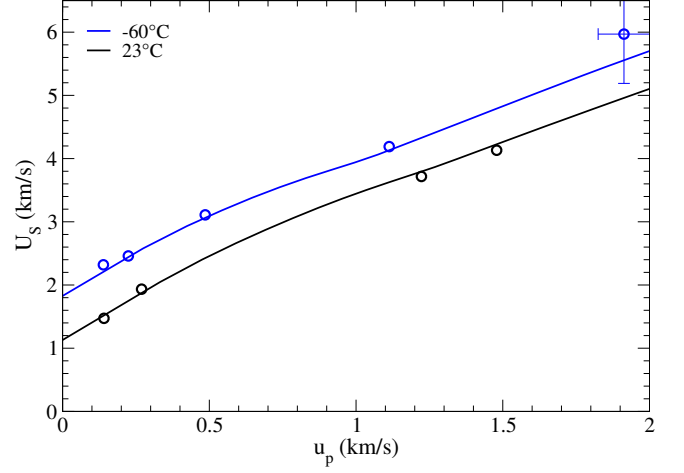


FIG. 2. Hugoniot results in the $U_S - u_p$ plane for SESAME 97990 as compared with data. Uncertainty analysis of the room temperature points is ongoing,¹⁷ those of the -60°C points are indicated only where greater than the symbol sizes.

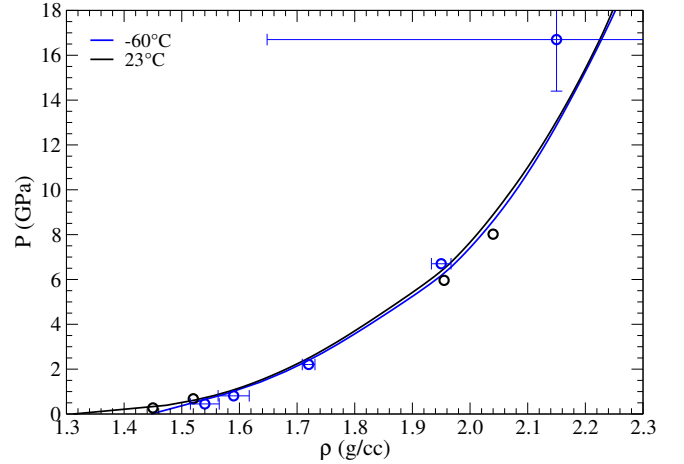


FIG. 3. Hugoniot results in the $P - \rho$ plane for SESAME 97990 as compared with data. Uncertainty analysis of the room temperature points is ongoing,¹⁷ those of the -60°C points are indicated only where greater than the symbol sizes.

mild structure visible at particle velocities $u_p \sim 0.7 - 1$, due to the low value chosen for η_{hi} and the resultant transition of the cold curve to TFD.

III. SUMMARY

We've outlined the construction of a new SESAME table for DC745U. Agreement with all data are good,^{4,8,21,22} although recovery of the highest pressure shock points is a little artificial. We should also mention that DC745, like other polymers, will decompose under sufficient load.²³⁻²⁷ This would most likely entail abrupt changes in volume and compressibility, and the resultant products mixture would be better described by

thermochemical modeling.²⁸ Both of these caveats should be revisited if accuracy at higher pressures proves unsatisfactory.

- ¹R. S. Maxwell, S. C. Chinn, J. Herberg, C. Harvey, C. Alviso, A. Vance, R. Cohenour, M. Wilson, and D. Solyom, “Baseline and lifetime assessments for DC745U elastomeric components,” Technical Report UCRL-TR-208929 (Lawrence Livermore National Laboratory, 2005).
- ²G. Spellman, “Polymeric peer review issues,” Presentation (Lawrence Livermore National Laboratory, 2002).
- ³R. S. Maxwell, S. C. Chinn, R. Gee, B. Balazs, N. Lecevic, J. Herberg, E. Gjerson, M. Patel, H. Wheeler, and M. Wilson, “Reassessing polymer lifetime prediction methods with improved characterization and diagnostics,” in *Polymer Durability and Radiation Effects*, ACS Symposium Series, edited by e. a. Celina, Mathew C. (American Chemical Society, Washington, D.C., 2007).
- ⁴D. Ortiz-Acosta, “Historical material analysis of DC745U pressure pads,” Technical Report LA-UR-12-23612 (Los Alamos National Laboratory, 2012).
- ⁵D. Ortiz-Acosta, “Solid silicone elastomer material(DC745U)-historical overview and new experimental results,” Technical Report LA-UR-12-23948 (Los Alamos National Laboratory, 2012).
- ⁶D. Ortiz-Acosta, “Low temperature studies on DC745U pressure pads,” Technical Report LA-UR-13-25885 (Los Alamos National Laboratory, 2013).
- ⁷D. Ortiz-Acosta, M. T. Janicke, J. Yoder, and C. M. Cady, “Post-cure studies on solid silicone elastomer: DC745U,” Technical Report LA-UR-14-20314 (Los Alamos National Laboratory, 2014).
- ⁸A. B. Goodbody, D. M. Dattelbaum, R. L. Gustavsen, B. D. Bartram, and D. B. Stahl, “Plate impact experiments on the silicone elastomer dc745u cooled to -60c,” AIP Conference Proceedings **1979**, 090004 (2018), <https://aip.scitation.org/doi/pdf/10.1063/1.5044861>.
- ⁹R. Menikoff, “Complete Mie-Grüneisen Equation of State,” Tech. Rep. LA-UR-12-22592-rev (Los Alamos National Laboratory, 2012).
- ¹⁰B. I. Bennett, “On Obtaining the Zero-Temperature Equation of State from Shock Data,” Tech. Rep. LA-9890-MS (Los Alamos National Laboratory, 1984).
- ¹¹R. P. Feynman, N. Metropolis, and E. Teller, Phys. Rev. **75** (1949).
- ¹²R. D. Cowan and J. Ashkin, Phys. Rev. **105** (1957).
- ¹³Ref. 11 describes the basic algorithm for Thomas-Fermi, and Ref. 12 describes the exchange contribution. However, what is actually implemented in OpenSesame is described Appendix A of Ref. ? , which differs from Ref. 12 in its use of a zero-temperature expression for exchange at *all* temperatures.
- ¹⁴See reference ? , section III-G.
- ¹⁵E. D. Chisolm, “Sesame 96170, a solid-liquid equation of state for ceo₂,” Tech. Rep. LA-UR-12-21066 (Los Alamos National Laboratory, 2012) rev. 2.
- ¹⁶That is, models where the zero point energy vanishes in the limit of zero density: $E(0,0) = 0$. This isn’t really appropriate for most soft materials such as DC745, whose constituent elements in their standard state exist as molecules (*e.g.*, H₂) having finite zpe even at zero density.
- ¹⁷D. M. Dattelbaum, Los Alamos National Laboratory, unpublished.
- ¹⁸B. Wunderlich, *Thermal Analysis of Polymeric Materials* (Springer, Berlin, 2005).
- ¹⁹J. D. Johnson, “A generic model for the ionic contribution to the equation of state,” High Pressure Research **6**, 277–285 (1991), <https://doi.org/10.1080/08957959108203212>.
- ²⁰D. C. Wallace, *Statistical Physics of Crystals and Liquids: A Guide to Highly Accurate Equations of State* (World Scientific Pub. Co. Inc., 2003).
- ²¹Denisse Ortiz-Acosta, Los Alamos National Laboratory, unpublished.
- ²²“Dow Corning 745U,” Tech. Rep. 5594 (Datapoint Labs, 2002).
- ²³C. E. Morris, J. N. Fritz, and R. G. McQueen, “The Equation of State of Polytetrafluoroethylene to 80 GPa,” J. Chem. Phys. **80**, 5203–5218 (1984).
- ²⁴C. E. Morris, E. D. Loughran, G. F. Mortensen, G. T. Gray III, and M. S. Shaw, “Shock Induced Dissociation of Polyethylene,” Shock Compression of Condensed Matter , 687–690 (1989).
- ²⁵D. M. Dattelbaum, J. D. Coe, C. B. Kiyanda, R. L. Gustavsen, and B. M. Patterson, “Reactive, Anomalous Compression in Shocked Polyurethane Foams,” J. Appl. Phys. **115**, 174908 (2014).
- ²⁶D. M. Dattelbaum, J. D. Coe, P. A. Rigg, R. J. Scharff, and J. T. Gammel, “Shockwave Response of Two Carbon Fiber-Polymer Composites to 50 GPa,” J. Appl. Phys. **116**, 194308 (2014).
- ²⁷D. M. Dattelbaum and J. D. Coe, “Shock-driven decomposition of polymers and polymeric foams,” Polymers **11** (2019), 10.3390/polym11030493.
- ²⁸W. R. Smith and R. W. Missen, *Chemical reaction equilibrium analysis: theory and algorithms* (Wiley, New York, 1982).